

REMARKS

Claim 1 has been amended, claim 6 has been cancelled, and claims 21-24 have been added. No new matter has been added by virtue of the amendments. For instance, support for the amendments appears on pages 8 and 12 of the application.

Applicants respond to the prior Office Action as follows.

Claims 1-12 were rejected under 35 U.S.C. 112, first paragraph. As grounds for the recitation of “propylene glycol diacetate” in claim 1 is noted.

By virtue of amendments made herein, claim 1 does not recite “propylene glycol diacetate”. It is thus believed the rejection has been obviated.

Claims 1-12 were rejected under 35 U.S.C. 112, second paragraph. The position is taken that the improper Markush language is recited in claim 1.

While Applicants respectfully disagree with the rejection, claim 1 has been amended as recommended in the Office Action. Reconsideration and withdrawal of the rejection is therefore requested.

Claims 1-5 and 7-11 were rejected under 35 U.S.C. 102(e) by Chung et al. (U.S. Patent 6,355,749).

Claims 1, 2, 4, 5 and 7-12 were rejected under 35 U.S.C. 102 over Nishi et al. (U.S. Patent 5,541,747) in view of Chung et al. (U.S. Patent 6,355,749).

Claims 1-5 and 7-12 were rejected under 35 U.S.C. 103 over Ohigashi et al. (U.S. Patent 5,679,753) in view of Chung et al. (U.S. Patent 6,355,749).

For the sake of brevity, the three rejections are addressed in combination.

While Applicants disagree with these rejections, it is also believed these rejections are obviated by the amendments made herein. In particular, independent claim 1 (the only pending independent claim) has been amended to incorporate features of former claim 6, which former claim was not rejected over the above relied-upon documents.

In view thereof, reconsideration and withdrawal of the rejections are requested.

Claims 1-12 were rejected under 35 U.S.C. 103 over Zhang et al. (U.S. Patent 6,423,412) in view of Chung et al. (U.S. Patent 6,355,749). The rejection is traversed.

The cited documents themselves specifically *teach against* the proposed combination. Thus, at column 2, line 37 through column 3, line 10, Chung et al. specifically addresses and distinguishes Zhang et al. [citing to WO 99/26261 (copy enclosed) which is the corresponding International application of Zhang et al. (U.S. Patent 6,423,412)].

In view of such disclosure of Chung et al., the skilled worker clearly would not have had type of incentive to equate and substitute solvents as proposed in the Office Action.

Additionally, none of the solvents recited in Applicants' claims 21 through 24 are mentioned or otherwise addressed in the Office Action.

Indeed, while Applicants fully believe that a *prima facie* case under 35 U.S.C 103 has not been presented by the cited documents, it is also believed that comparative data of record fully rebuts any *prima facie* case that may be contended to exist. In this regard, attention is directed to the comparative results disclosed at page 12 and Figure 2, which show *inter alia* notable results

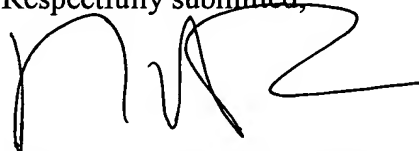
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for ethyl lactate and propylene glycol methyl ether acetate. Those solvents are recited in claims 23 and 24, as well as the other pending claims.

In view thereof, reconsideration and withdrawal of the rejection are requested.

It is believed the application is in condition for immediate allowance, which action is earnestly solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to be 'P. Corless', written over the typed name.

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(21) International Application Number: PCT/US98/24593 (22) International Filing Date: 18 November 1998 (18.11.98) (30) Priority Data: 60/065,641 18 November 1997 (18.11.97) US 60/093,718 22 July 1998 (22.07.98) US (71) Applicant: THE PENN STATE RESEARCH FOUNDATION [US/US]; 304 Old Main, University Park, PA 16802 (US). (72) Inventors: ZHANG, Qiming; 548 Westgate Drive, State College, PA 16803 (US). BHARTI, Vivek; Apartment 39, 210 E. Hamilton Avenue, State College, PA 16801 (US). (74) Agent: MONAHAN, Thomas, J.; Intellectual Property Office, The Pennsylvania State University, 113 Technology Center, University Park, PA 16802 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FERROELECTRIC RELAXOR POLYMERS (57) Abstract The invention is embodied in an electrical device which includes at least a layer of a ferroelectric polyvinylidene fluoride polymer that has been processed to exhibit an electrostrictive strain of 4 % or more when an electric field gradient of 50 megavolts per meter or greater is applied thereacross. The processing of the polymer preferably involves subjecting it to either electron beam radiation or gamma radiation. The polyvinylidene fluoride polymer is selected from the group of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene fluoride tetrafluoroethylene P(VDF-TFE), polyvinylidene fluoride trifluoroethylene-hexafluoropropylene P(VDF-TFE-HFE) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE).		

FERROELECTRIC RELAXOR POLYMERS

This Application claims priority from U. S. Provisional Application Serial No. 60/065,641, filed November 18, 1997, and Provisional Application Serial No. 60/093,718, filed July 22, 1998.

FIELD OF THE INVENTION

10 This invention relates to ferroelectric polymers and, more particularly, to relaxor ferroelectric polymers that have been processed to exhibit high electrostrictive strain levels.

15 BACKGROUND OF THE INVENTION

Ferroelectric polymers have attracted interest for many years as they reveal a new aspect of polymers for use as functional materials. Such polymers have been 20 recognized for their potential uses in a variety of large area transducer, actuator and sensor applications because of their flexibility, mechanical strength, light weight, easy processibility into large area films and ability to be arranged into desirable configurations. By contrast, 25 existing functional materials, such as ceramics, are brittle, heavy and difficult to produce into large area configurations.

In spite of their advantages over the ceramics, 30 current polymers suffer low field sensitivities, such as dielectric constant, piezoelectric coefficient,

electromechanical coupling factor and field induced strain. These constraints severely limit the application of ferroelectric polymers as transducers, sensors and actuators.

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There is a demand for improved materials for use in actuators and transducers due to the limitations of currently available materials. For example, current actuator materials, such as electrostatic, 10 electromagnetic and piezoelectric materials, exhibit limitations in one or more of the following performance parameters: strain, elastic energy density, speed of response and efficiency. For instance, piezoceramic and magnetostrictive materials, while possessing low 15 hysteresis and high response speeds, suffer from low strain levels ($\sim 0.1\%$). Shape memory alloys generate high strain and high force but are often associated with large hysteresis and very slow response speeds. On the other hand, there are several polymers such as polyurethane, 20 polybutadiene etc. which can generate high electric field induced strain i.e. up to 6-11%. But, due to their low elastic modulus, their elastic energy density is very low. Further, the strain generated in these materials is mainly due to the electrostatic effect, which is a low 25 frequency process. Use of these materials at high frequencies reduces their response drastically. In addition, due to their low dielectric constant, the electric energy density and electromechanical coupling coefficient of these polymers is very low which is an 30 undesirable characteristic for many transducer and actuator applications.

Substantial efforts have been devoted to improvement of phase switching materials where an antiferroelectric and ferroelectric phase change can be field induced to
5 cause a high strain in the material. While strains higher than 0.7% have been achieved in such materials, due to the brittleness of ceramics, severe fatigue has been found to occur at high strain levels. Recently, in a single crystal ferroelectric relaxor, i.e., PZN-PT, an
10 electric field strain of about 1.7%, with very little hysteresis, has been reported, which is exceptionally high for an inorganic materials (see: Park and Shrout, J Appl. Phys., 82, 1804 (1997)). In such ceramic materials, mechanical fatigue occurs at high strain
15 levels, a major obstacle limiting their use for many applications.

For many applications, such as microrobots, artificial muscles, vibration controllers, etc., higher
20 strain levels and higher energy densities are required. Thus, there is a need for a general purpose electroactive material with improved performance for use with transducer and actuators.

25 There is a further requirement for improved ultrasonic transducers and sensors for use in medical imaging applications and low frequency acoustic transducers. Current piezoceramic transducer materials, such as PZTs, have a large acoustic impedance ($Z > 35$
30 Mrayls) mismatch with the air and human tissue ($Z < 2$ Mrayls). On the other hand, piezoelectric polymers such

as P(VDF-TrFE), PVDF not only have an acoustic impedance well matched ($Z < 4$ Mrayls) to human tissue but also offer a broad nonresonant frequency bandwidth. But, because of their low piezoelectric activity and low coupling coefficient, the sensitivity of such ultrasonic polymer transducers is very low.

The capacitor industry also requires a capacitor which has a much higher electric energy density than is currently available. Current dielectric materials, such as polymers, have a low dielectric constant ($\sim 2-10$) and limited energy density. In addition, with current ceramics, the maximum field which can be applied is limited.

15

Accordingly, it is an object of the invention to provide a polymeric material which can generate a high electric field- induced strain with little hysteresis.

It is another object of the invention to provide a polymeric material which exhibits a high elastic energy density.

It is a further object of the invention to provide a polymer in which the direction of induced strain can be tuned by means of alteration of the ratio of transverse strain (S_1) to longitudinal strain (S_3).

It is yet another object of the invention to provide a polymeric material that exhibits a room temperature dielectric constant that is higher than other currently

available polymers.

It is a further object of the invention to provide a polymer which exhibits relaxor ferroelectric behavior and hence has a slim polarization hysteresis loop which, coupled with high electric field breakdown strength, can provide a capacitor with high electric energy density.

SUMMARY OF THE INVENTION

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The invention is embodied in an electrical device which includes at least a layer of a ferroelectric polyvinylidene flouride polymer that has been processed to exhibit an electrostrictive strain of 4% or more when an electric field strength of 50 megavolts per meter or greater is applied thereacross. The processing of the polymer preferably involves subjecting it to either electron beam radiation or gamma radiation. The polyvinylidene flouride polymer is selected from the group of: polyvinylidene flouride, polyvinylidene flouride-trifluoroethylene P(VDF-TrFE), polyvinylidene tetrafluoroethylene P(VDF-TFE), polyvinylidene trifluoroethylene hexafluoropropylene P(VDF-TFE-HFE) and polyvinylidene hexafluoropropylene P(VDF-HFE).

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a plot of polarization P versus electric field E showing polarization hysteresis loops of P(VDF-TrFE) 50/50 copolymer measured at room temperature: (a) before irradiation and (b) Irradiation with 40 Mrad at

30

120C.

Fig. 2a is a plot of longitudinal strain versus applied electric field showing the field dependence of
5 P(VDF-TrFE) 65/35 mol% unstretched copolymer film after irradiation at 120C with 60 Mrad dose.

Fig. 2b is a plot of longitudinal strain versus applied electric field for P(VDF-TrFE) (50/50 mol%)
10 unstretched film after irradiation at 120C with 40 Mrad dose.

Fig. 3 is a plot of the electrostrictive relation between the strain and polarization shown in Fig. 2,
15 where the strains at $P > 0$ and $P < 0$ regions are overlapped as a result of the dependence of P^2 on the strain. The deviation of the data points from the straight line at S near zero is due to the zero point uncertainty of the measurement set-up.

20

Figs. 4a and 4b illustrate plots of strain versus electric field of P(VDF-TrFE) (65/35 mol%) copolymer films, where plot (B) shows longitudinal strain of stretched film treated the same as in (A). (A) shows
25 transverse strain of stretched films irradiated at different temperatures with different doses.

Fig. 5 is a plot of strain versus electric field of P(VDF-TrFE) (65/35 mol%) unstretched films, irradiated at
30 120C with 60 Mrad dose showing that the longitudinal strain (S_3) is three times higher than transverse strain

(S1).

Fig. 6 illustrates plots of strain versus electric field of P(VDF-TrFE) (65/35 mol%) copolymer films, where
5 plot (A) shows longitudinal strain of stretched and unstretched films irradiated at 120C with different doses.

Fig. 7a incorporates Table 1 which indicates effects
10 of irradiation parameters on unstretched P(VDF-TrFE) copolymer films.

Fig. 7b incorporates Table 2 which indicates effects of irradiation parameters on stretched P(VDF-TrFE)
15 copolymer films in a nitrogen atmosphere.

Fig. 7c incorporates Table 3 which compares strain and strain energy densities for a variety of materials.

20 Fig. 8 is a plot of variation of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) (50/50 mol%) versus temperature for unstretched, unirradiated copolymer film at 50 Hz, 100 Hz, 1KHZ, 0.1KHz, 0.4KHz and 1MHz frequencies.

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Fig. 9 is a plot of variation of dielectric constant K(solid lines) and dielectric loss $\tan \delta$ (dashed lines) as a function of temperature for unstretched P(VDF-TrFE) (50/50 mol%) copolymer films irradiated at 120C with 40
30 Mrad dose. The measuring frequencies (from top to bottom for dielectric constant and from bottom to top for

dielectric loss) were 50 Hz, 100 Hz, 1KHZ, 0.1KHz, 0.4KHz and 1MHz.

Fig. 10 is a plot of dielectric constant K measured at 1 kHz with respect to temperature for (A) unirradiated and (B) irradiated stretched, P(VDF-TrFE) (65/35 mol%) copolymer films irradiated at 95°C with 60 Mrad dose, (where the data were taken during sample heating and cooling).

10

Fig. 11 is a plot of dielectric constant K versus temperature measured at 1 kHz frequency for stretched P(VDF-TrFE) (65/35 mol%) copolymer films irradiated at 95C with (A) 40, (B) 60, (C) 80, (D) 100, (E) 120 Mrad irradiation doses, (where the data were taken during sample heating and cooling).

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Fig. 12 is a plot of dielectric constant K (solid lines) and dielectric loss Tan ((dashed lines) versus temperature measured at 1 kHz frequency for unstretched P(VDF-TrFE) (50/50 mol%) copolymer films irradiated at (A) 120C with 40 Mrad dose (B) 25C with 80 Mrad.

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Fig. 13 is a plot of dielectric constant K (solid lines) and dielectric loss Tan ((dashed lines) as a function of temperature at 1 kHz frequency for stretched P(VDF-TrFE) (65/35 mol%) copolymer films irradiated at 95C with 40 Mrad dose, (where the data were taken during sample heating and cooling).

25

30

Fig. 14 is a plot of change in polarization

hysteresis loops with the noted temperatures for P(VDF-TrFE) (50/50 mol%) copolymer films irradiated at 120°C with 40 Mrad.

5 Fig. 15 is a schematic of a bimorph actuator employing a polymer processed in accord with the invention.

10 Fig. 16 is a schematic of a multilayer capacitor employing polymer layers processed in accord with the invention.

DETAILED DESCRIPTION OF THE INVENTION

15 In ferroelectric polymers such as P(VDF-TrFE), it has been found during structural investigations that large lattice strains and large changes in dimensions are produced when a phase transformation from ferroelectric phase to paraelectric phase occurs. See: T. Furukawa,
20 Phase Transition, 18, 143 (1989); K. Tashiro et al.

It has been observed by others in studies of polyvinylidene fluoride-tri-fluoroethylene P(VDF-TrFE) copolymers, that high energy irradiation can convert the
25 ferroelectric phase into a paraelectric phase. See A.J. Lovinger, Macromolecules, 18, 910 (1985) and F. Macchi et al., Nucl. Instr. and Methods in Phys. Res., B46, 324 (1990); Ferroelectrics, 109, 303 (1990). Macchi et. al. observed changes in dielectric constant, elastic
30 properties and thermal expansion after irradiation and correlated their results to changes in crystallinity.

Ferroelectrics, 57, 297 (1984); T. Yamada et al., J. Appl. Phys., 52, 948 (1981); and A. J. Lovinger et al., Polymer, 28, 617 (1987).

5 In addition, due to the presence of the crystalline phase, the Young's modulus of these polymers is very high and offers high force levels and high energy densities. These results demonstrate that ferroelectric polymers can provide an effective coupling between an applied electric
10 field and a resultant strain response.

 However, a problem exists in utilizing the strain associated with phase transformation in existing ferroelectric polymers. In particular, the problem is
15 that the transition is very sharp and occurs at high temperatures. Further, the transition exhibits a large hysteresis.

 The information developed by Macchi et al. and
20 Lovinger served as a foundation for Applicants' study that led to this invention. Applicants examined the effects of irradiation on the field induced strain level, the elastic energy density and degree of hysteresis by (i) change of irradiation parameters (such as irradiation
25 dose and temperature), (ii) use of different sample processing techniques (such as melt pressing and solution casting using different solvents, annealing temperature and time) and (iii) use of different mol%'s of P(VDF-TrFE) copolymer. All irradiation of polymers was carried
30 out in inert atmospheres, e.g., nitrogen or argon, to prevent oxidation of the samples.

It was found that under certain sample treatment conditions (irradiation dose, irradiation temperature, film preparation methods etc.), an ultra-high
5 electrostrictive strain and a high elastic energy density can be obtained. Tested polymers can withstand an electric field higher than 350 MV/m, resulting in very high elastic energy densities. It was also found that the phase which was transformed after electron
10 irradiation is not a simple paraelectric phase, but a relaxor ferroelectric which has local micropolar regions.

Applicants were able to modify the structure of ferroelectric polymers so that use could be made of the
15 strains associated with phase transition at room temperature and to either reduce or eliminate the hysteresis losses, without reducing the strain levels. It was found that this was possible if the macroscopic coherent polarization domains could be broken up and
20 inhomogeneities/defects introduced into the crystal structure, i.e., conversion of part of the trans molecular bonds to gauche molecular bonds.

There are several ways by which these effects can be
25 accomplished, i.e., chemically, by adding a bulky side group to the main polymer chain which operates as an internal plasticizer; and by irradiation, i.e., by introducing defects using high energy radiation (e.g. at energy levels in an approximate range of 500 KeV to 3MeV)
30 using beta or gamma rays in an oxygen free atmosphere. The radiation, in addition to inducing defects in the

molecular structures, also enabled crosslinking to occur.

In addition to P(VDF-TrFE), it is clear that additional polyvinylidene fluoride polymers such as
5 polyvinylidene fluoride tetrafluoroethylene P(VDF-TFE),
polyvinylidene fluoride trifluoroethylene -
hexafluoropropylene P(VDF-TFE-HFE), polyvinylidene
fluoride - hexafluoropropylene P(VDF-HFE) etc., can be
processed to exhibit very high field-induced strains.
10 Hereafter, the term "PVDF" will be used to collectively
refer to the aforementioned homopolymer and copolymers.

Using radiation to introduce defects into the
polymeric materials, it was found that energy levels in
15 the approximate range of 500 KeV to 3MeV were usable,
although energy levels higher than 500 KeV were
preferred. The radiation sources were preferably electron
beams, and gamma rays from suitable radioactive species
(e.g., cobalt).

20

Further, it was found that both stretched and
unstretched polymeric species exhibited high levels of
induced strain, with stretched polymers modified in
accord with the invention being preferred for actuator
25 applications with actuation along the stretching
direction and unstretched polymers, modified in accord
with the invention, being preferred for capacitor
applications (along the thickness direction).

30 Film preparation and irradiation conditions:

Polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymers were used during the experimental investigations described below, however it is to be understood that other polymers may be similarly processed to achieve similar results, as indicated above. Copolymer powders having PVDF(x) - TrFE(1-x), where x ranges from 50 to 86 mol %, were supplied by Solvay and Cie, Belgium. Polymer films were prepared by both melt pressing and solution casting methods. In case of melt pressed films, at first, the copolymer powder was pressed between two aluminum foil layers at temperatures between 180C to 220C and then cooled to room temperature, either by quenching the sandwich in ice cooled liquid or by slow cooling.

For solution cast films, the powder was dissolved either in N,N-dimethyl formamide (DMF) or methyl ethyl ketone (MEK) solutions. These solutions were poured onto an ultrasonically cleaned glass plate, placed in an oven and maintained at 30C or 70C for six hours, in case of MEK and DMF solutions, respectively. After slow evaporation of the solvents, uniform transparent films of P(VDF-TrFE) were formed.

Stretched films were prepared by uniaxially stretching the films up to five times their initial length, at temperatures between 25C ~ 50C. In order to improve the crystallinity and to remove residual solvent in case of solution cast films, both unstretched and stretched films (under clamped conditions) were annealed in a vacuum oven at 140C for 16 hours. The films were then irradiated in an oxygen free atmosphere (e.g.,

nitrogen or argon) with 2.5 MeV to 3 MeV electrons at different temperature ranges from 25 to 120C. Several irradiation dosages in the range from 30 to 175 Mrad were used.

5

Polarization Behavior:

It was found that irradiation parameters greatly affected the polymers' material properties. Thus, selection of irradiation condition was important to obtain a polymeric material with desired electrical properties. The changes in saturation polarization P_s , remnant polarization P_r and critical field E_c , observed from polarization hysteresis loops measured at room temperature, are shown in Figs. 7b and 7c (Tables 2 and 3). P_s , P_r and E_c are saturation polarization, remnant polarization and critical field, respectively, observed from ferroelectric hysteresis loops measured at 150 MV/m electric field.

20

It was discovered that by irradiating the copolymer under proper irradiation conditions, the ferroelectric hysteresis was eliminated. This effect is shown in Fig. 1 which plots polarization P versus electric field E and shows polarization hysteresis loops of P(VDF-TrFE) 50/50 copolymer, measured at room temperature: (a) before irradiation and (b) after irradiation with 40 Mrad at 120C.

30 Strain data:

A large increase was observed in electric field-induced strain for both stretched and unstretched films along and perpendicular to the applied electric field (i.e., longitudinal strain S_3 and transverse strain S_1) (along the stretching direction in case of stretched films). Fig. 2b is a plot of longitudinal strain versus applied electric field for a P(VDF-TrFE) (50/50 mol%) unstretched film irradiated with 40 Mrad at 120°C. Fig. 2b is a plot of longitudinal strain versus applied electric field showing the field dependence of P(VDF-TrFE) 65/35 mol% unstretched copolymer film after irradiation at 120°C with 60 Mrad dose.

As there shown, the maximum longitudinal strain levels, 4% and 4.5 % were observed at 150 and 190 MV/m for P(VDF-TrFE), 50/50 and 65/35 mol % unstretched films respectively. In addition, as shown in Fig. 4, the induced strain exhibited very low hysteresis and followed the electrostrictive relation, $S = QP^2$ between strain (S) and applied electric field (E). Q is an electrostrictive coefficient. The electrostrictive strain was reproducible under a cyclic electric field. The preferred molar percentages of the monomers in P(VDF-TrFE) are from about 30/70 mol % to about 75/25 mol %.

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This attribute is an attractive feature for many transducer applications, for example, displacement transducers are used in optical communications to control optical path lengths with accuracy's on the order of a wavelength of light.

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An outstanding characteristic of materials made according to the invention is that by modifying the polymer morphology (stretched vs unstretched) and controlling the irradiation parameters, the magnitude and direction of the transverse and longitudinal strain can be tuned.

For example, for stretched films, the transverse strain is 0.8 to 1.2 times the longitudinal strain. This is shown in Fig. 4 which illustrates plots of strain versus electric field of P(VDF-TrFE) (65/35 mol%) copolymer films, where plot (A) shows longitudinal strain of stretched and unstretched films irradiated at 120C with different doses and plot (B) shows transverse strain of stretched films irradiated at different temperatures with different radiation.

In unstretched films, the transverse strain is about 0.2 to 0.4 times the longitudinal strain (with an opposite sign). This is shown in Fig. 5 which is a plot of strain versus electric field of P(VDF-TrFE) (65/35 mol%) unstretched films, irradiated at 120C with 60 Mrad dose, showing that longitudinal strain (S_3) is three times higher than transverse strain (S_1).

25

However, strain measured perpendicular to the stretching and applied field direction is always smaller than the strain measured along the field direction (longitudinal strain, S_3) and the strain measured along the stretching direction (transverse strain, S_1).

30

The effect of irradiation parameters are shown in Figs. 4 and 5. As is apparent from Fig. 6 for certain samples, the ratio of the strain level to electric field is higher in comparison to others. The other samples for which the ratio of strain to field was higher were selected for piezoelectric coefficient measurements. The maximum measured piezoelectric coefficients were $d_{33} = -350$ pC/N and $d_{31} = 260$ pC/N. Those measured values are almost 10 times higher than the values reported for prior art P(VDF-TrFE) copolymers and are almost comparable to the piezoelectric ceramic PZT-5H.

A material with such a high piezoelectric coefficient, a high electrostrictive strain level, with a further ability to control the strain magnitude and direction is an attractive candidate for actuator, transducer and sensor applications. However, many soft polymers can also generate very high strain levels due to the electrostatic effect. Therefore, in addition to the strain level, other parameters such as, the volumetric ($Ysm^2/2$) and gravimetric ($Ysm^2/2()$) strain energy densities and blocking force levels should be used in order to evaluate the actuator material's performance.

Table 1 (see Fig 7a) compares a copolymer prepared in accord with the invention with several currently known materials including the ferroelectric relaxor single crystal PZN-PT, which was discovered recently to possess an ultrahigh strain response. As can be seen, the P(VDF-TrFE) copolymer exhibits the maximum elastic energy density.

Dielectric results:

The dielectric constant of an electrostrictive
5 polymeric material prepared in accord with the invention
also shows a remarkable increase at room temperature,
after irradiation. Fig. 8 plots variations of dielectric
constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) versus temperature for unstretched, non-
10 irradiated copolymer film at 50 Hz, 100 Hz, 1KHz, 0.1KHz,
0.4KHz and 1MHz frequencies. Fig. 9 plots variations of
dielectric constant K (solid lines) and dielectric loss
 $\tan \delta$ (dashed lines) as a function of temperature for
unstretched P(VDF-TrFE) (50/50 mol%) copolymer films,
15 irradiated at 120C with 40 Mrad dose. The measuring
frequencies (from top to bottom for dielectric constant
and from bottom to top for dielectric loss) were 50 Hz,
100 Hz, 1KHz, 0.1KHz, 0.4KHz and 1MHz.

20 Comparing the non-irradiated material (Fig. 8) and
the irradiated material (Fig. 9) the dielectric constant
of unstretched 50/50 copolymer, at room temperature, for
the irradiated film is higher than the non-radiated
material. After irradiation, the dielectric transition
25 peak becomes broader and shifts towards lower
temperatures.

Similar to strain, the dielectric constant also can
be adjusted by using different material processing
30 conditions and irradiation parameters. Fig. 10 is a plot
of dielectric constant K measured at 1 kHz with respect

to temperature for stretched, P(VDF-TrFE) (65/35 mol%)
copolymer films (A) unirradiated, (B) irradiated at 95C
with 60 Mrad dose. As can be seen by comparing the
dielectric constant for the unirradiated and irradiated
5 stretched P(VDF-TrFE) (65/35 mol%) film, the dielectric
constant for the stretched irradiated films is higher
than the unirradiated films.

Again by controlling the irradiation parameters, the
10 dielectric constant can be tailored. Fig. 11 shows this
effect and illustrates that by increasing the irradiation
dose, the dielectric peak becomes broader, there is less
hysteresis and the dielectric constant decreases.
Further, as shown in Fig. 12, by increasing the
15 irradiation temperature, the irradiation dose can be
reduced significantly.

Fig. 13 illustrates that a maximum dielectric
constant of about 67 and a loss in the range of 1- 2% was
20 observed at 1 kHz (near room temperature) in 65/35
stretched films irradiated at 95C for a 40 Mrad dose.

To Applicants' knowledge, a P(VDF-TrFE) copolymer
produced in accord with the invention exhibits a highest
25 dielectric constant (with low dielectric loss at room
temperature) among known polymer dielectric materials.
The same can be expected for other PVDF polymers.

It was found that a field of up to 350 MV/m can be
30 applied to a polymer prepared in accord with the
invention without causing breakdown. Accordingly, a

capacitor material results with an electric energy density of about 36 J/cm³.

Relaxor Behavior:

5

Irradiated polymer films prepared in accord with the invention exhibit a relaxor ferroelectric behavior. In comparison to normal ferroelectrics, relaxor ferroelectrics are characterized by the presence of diffuse and rounded maxima in the temperature dependence of their dielectric permittivity, and further exhibit a strong relaxation dispersion for a wide frequency range. In addition, relaxors show a slim polarization hysteresis loop near the dielectric maxima. But, as temperature is reduced from dielectric maxima (T_{\max}), the hysteresis loop gradually broadens and finally transforms into a regular rectangular loop at a temperature well below T_{\max} .

20 It was found that irradiated P(VDF-TrFE) shows a broad dielectric peak which shifts towards higher temperature with increasing frequency (see Fig. 9) and follows the Vogel-Fulcher law, an empirical law which is applicable for a system which undergoes relaxation freezing below certain temperatures. The square-to-slim hysteresis loop is evident in Fig. 14 which plots changes in polarization hysteresis with various temperatures for P(VDF-TrFE) (50/50 mol%) copolymer films irradiated at 120C with 40 Mrad. As can there be seen, the polarization behavior becomes hysteretic at -25C, with remnant polarization, $P_r = 2.1 \text{ mC/cm}^2$, saturation polarization, P_s

= 40 mC/cm² and critical field, $E_c = 45.5$ MV/m. However, with increases in temperature, the polarization reduces gradually and shows a slightly a non-linear polarization loop near 50C i.e. near T_{max} .

5

These results show that a material made in accord with the invention (i.e., after irradiation) behaves like a relaxor ferroelectric material (rather than a simple paraelectric, as reported earlier). The results obtained from X-ray scans, Raman spectra, DSC and crosslinking measurements show that electron irradiation breaks up the coherent polarization domains in the normal ferroelectric material to a nanoscale polar region, introduces defects randomly by introducing gauche bonds in long trans-planar polymer chains and causes crosslinking in the crystalline region. Due to large difference in the lattice constant between polar and non polar phases in a P(VDF-TrFE) copolymer, a gradual increase in the polarization with field in the electrostrictive copolymer produces a giant electrostrictive strain and strain energy density.

Electroactive polymer materials developed in accord with the invention show: very high strain (4-5%), high elastic energy density (above 0.3 J/cm³ or 160 J/kg), high dielectric constant with relatively low loss at room temperature (>40 at 1 kHz and a loss <5%), a slim polarization hysteresis loop at room temperature, a high piezoelectric response in a DC biased state and high electric energy density (a breakdown field >350MV/m).

30

Most importantly, being a polymeric material, their

acoustic impedance levels match human tissue and exhibit no mechanical fatigue at high strain levels. Further, their transverse strain S_1 can be tuned over a large range with respect to their longitudinal strain S_3 . S_1/S_3 can be
5 tuned from 0.2 to more than 1.1. Accordingly, an electrostrictive relaxor ferroelectric polymer prepared in accord with the invention exhibits improved electrical properties that offer substantial improvements in material characteristics required for capacitor, actuator
10 and transducer applications.

Figs. 15 and 16 illustrate examples of a bimorph actuator and a multilayer capacitor, both of which incorporate polymer layers that have been processed in
15 accord with the invention.

It should be understood that the foregoing description is only illustrative of the invention. Various alternatives and modifications can be devised by those
20 skilled in the art without departing from the invention. Accordingly, the present invention is intended to embrace all such alternatives, modifications and variances which fall within the scope of the appended claims.

CLAIMS

5 1. An electrical device including at least a layer
of a relaxor ferroelectric polymer that has been
processed to exhibit an electrostrictive strain, at room
temperature, of 4% or more when an electric field
gradient of about 100 megavolts per meter or greater is
10 applied thereacross.

 2. The electrical device as recited in claim 1,
wherein said relaxor ferroelectric polymer comprises a
polyvinylidene flouride polymer.

15 3. The electrical device as recited in claim 1,
wherein said polymer is selected from the group
consisting of: polyvinylidene flouride, polyvinylidene
flouride-trifluoroethylene P(VDF-TrFE), polyvinylidene
20 flouride tetrafluoroethylene P(VDF-TFE), polyvinylidene
flouride trifluoroethylene - hexafluoropropylene P(VDF-
TFE-HFE) and polyvinylidene flouride -
hexafluoropropylene P(VDF-HFE).

25 4. The electrical device as recited in claim 1,
wherein said electrical device is a capacitor.

 5. The electrical device as recited in claim 1,
wherein said electrical device is an actuator.

30 6. The electrical device as recited in claim 1

wherein said layer of relaxor ferroelectric polymer exhibits a stretched configuration.

7. The electrical device as recited in claim 1,
5 wherein said relaxor ferroelectric polymer is produced by the steps of:

a) producing a layer of a polyvinylidene flouride polymer; and

10

b) irradiating said layer with an energy beam having an equivalent energy level of at least 500 KeV, said energy level sufficient to induce one or more of structural defects or crosslinking in said layer.

15

8. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer exhibits a dielectric constant and a dielectric loss, at room temperature, of greater than 40 at 1kHz and higher, and
20 less than 5%, respectively.

9. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer exhibits an elastic energy density, at room temperature, of greater
25 than 0.3 Joules/cm³ or 160 Joules/kg.

10. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer exhibits an electric energy density, at room temperature, which
30 enables avoidance of breakdown at applied field levels thereacross of at least about 350 megavolts per meter.

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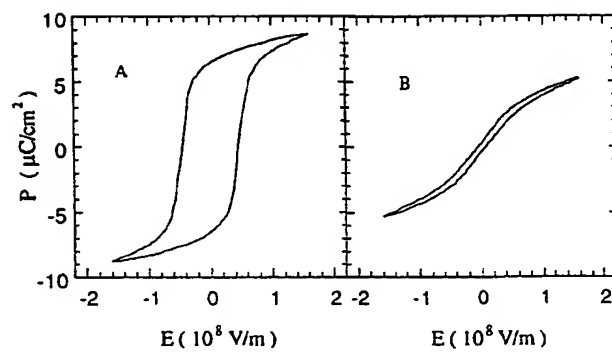


Figure - 1

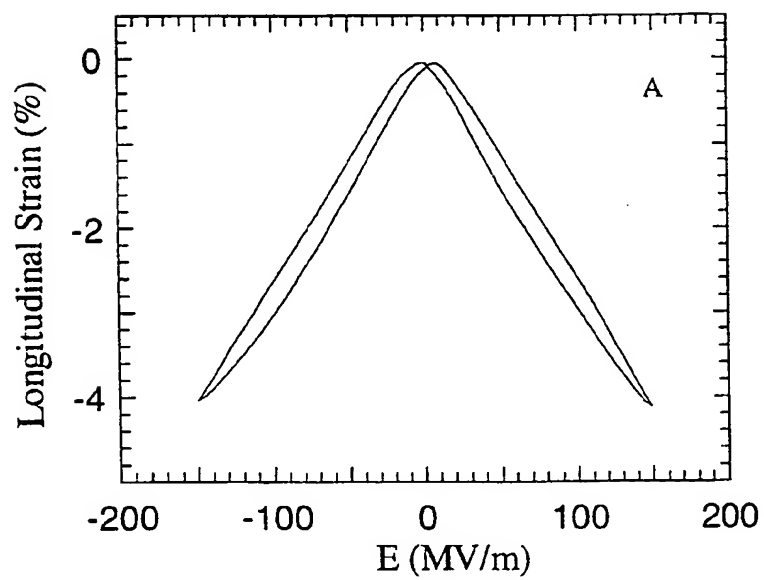


Figure - 2A

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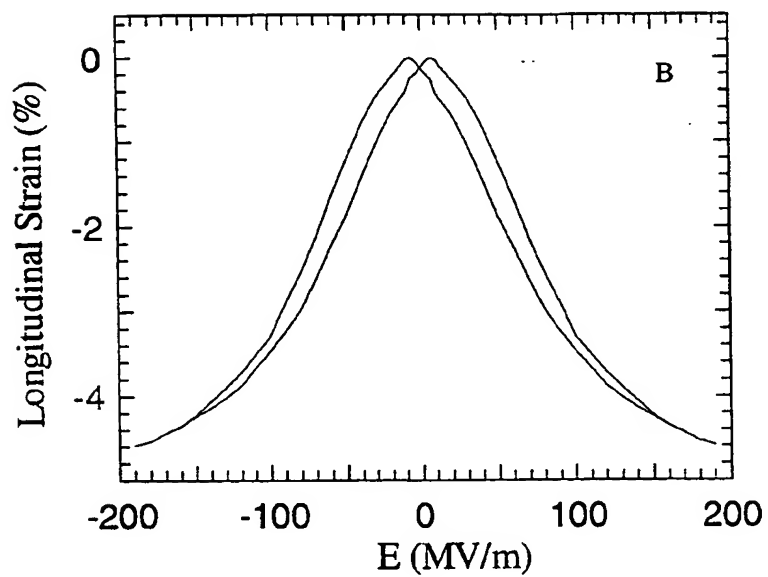


Figure - 2B

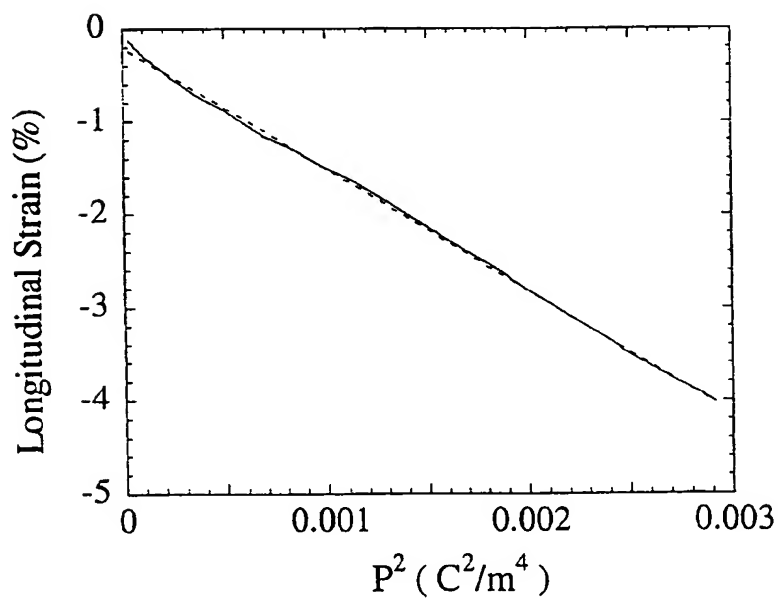


Figure - 3

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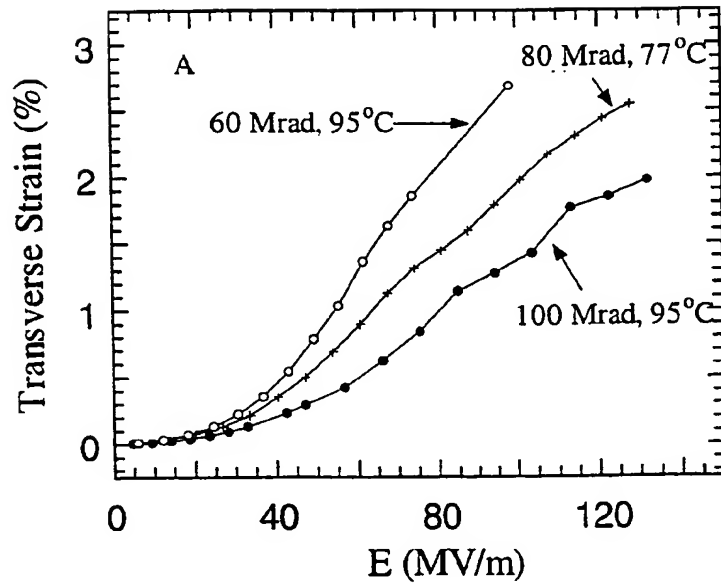


Figure - 4A

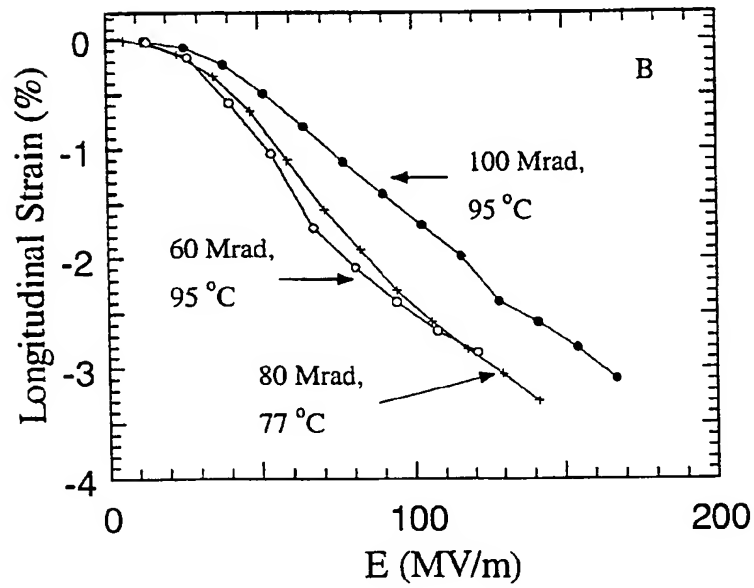


Figure - 4B

SUBSTITUTE SHEET (rule 26)

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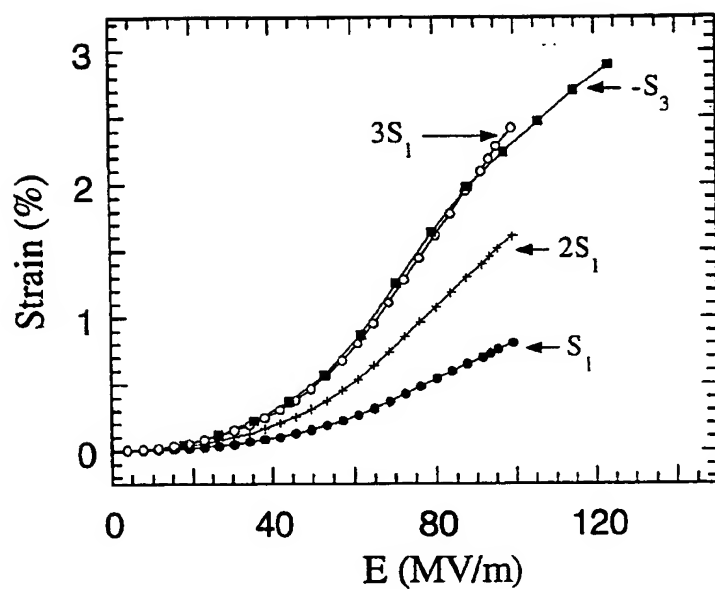


Figure - 5

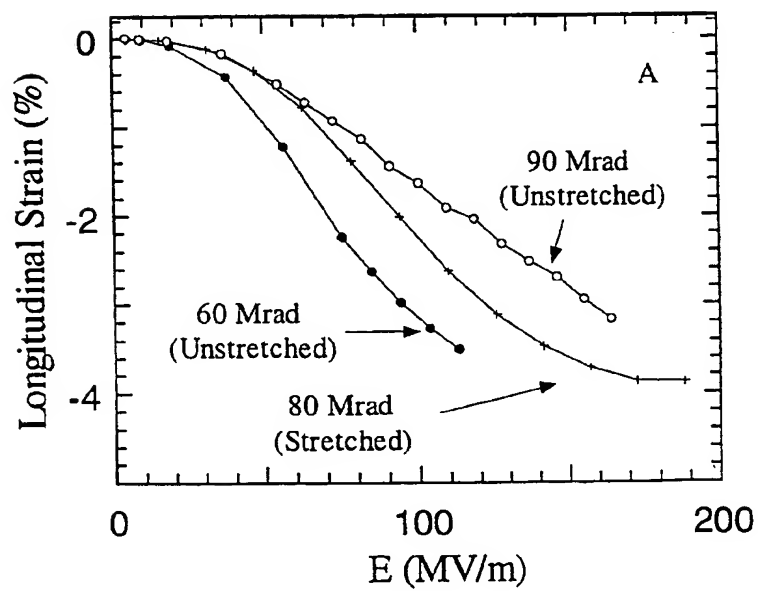


Figure - 6 A

SUBSTITUTE SHEET (rule 26)

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Table- 1
Comparison of Strain and Strain Energy Densities.

Materials		Y (GPa)	S _m (%)	YS _m ² /2 (J/cm ³)	YS _m ² /2ρ (J/kg)
Electrostrictive	S _j	0.40	4.5	0.4	200
PVDF-TrFE	S _i	1.3	3.5	0.8	400
Piezoceramics		64	0.2	0.13	17
Magnetostrictor		100	0.2	0.2	21.6
PZN-PT Single Crystal		7.7	1.7	1.0	131
Polyurethane		0.017	11	0.1	83

Figure - 7A

Table -2
PVDF-TrFE Stretched Samples Irradiated under Nitrogen Atmosphere.

Field Applied = 150 MV/m		Absorbed Dose (Mrad)						
		0	40	60	80	100	120	142.5
50/50 Irradiated at 77 °C	P _r (mC/m ²)	130.00	-	56.00	43.50	35.50	28.00	-
	P _r (mC/m ²)	113.26	-	4.18	2.87	2.55	2.56	-
	E _c (MV/m)	54.11	-	8.18	8.01	9.84	13.26	-
50/50 Irradiated at 95 °C	P _r (mC/m ²)	130.00	63.00	53.00	41.00	32.00	-	-
	P _r (mC/m ²)	113.26	5.41	3.54	2.61	3.98	-	-
	E _c (MV/m)	54.11	9.72	7.35	7.99	17.71	-	-
65/35 Irradiated at 77 °C	P _r (mC/m ²)	134.00	-	-	87.00	56.00	50.00	45.5
	P _r (mC/m ²)	117.57	-	-	13.18	3.96	2.79	4.0
	E _c (MV/m)	53.61	-	-	16.91	9.64	7.53	12.33
65/35 Irradiated at 95 °C	P _r (mC/m ²)	134.00	-	88.00	60.00	64.00	54.00	-
	P _r (mC/m ²)	117.57	-	18.59	3.91	6.54	6.13	-
	E _c (MV/m)	53.61	-	18.70	8.55	12.69	13.98	-

Figure - 7B

Table -3
Effect of Irradiation Parameters on unstretched P(VDF-TrFE) copolymer films.

Field Applied = 150 MV/m		Absorbed Dose (Mrad)														
		0	30	40	60	80	90	100	110	120	125	142.5	150	175		
50/50 Irradiated at 25 °C	P_1 (mC/m ²)	87.0				55		62.5		45						
	P_2 (mC/m ²)	64.4				3.94		3.0		3.1						
	E_1 (MV/m)	44.8				7.2		5.2		8.1						
50/50 Irradiated at 95 °C	P_1 (mC/m ²)	87.0		52.5	47	35										
	P_2 (mC/m ²)	64.4		5.43	4.75	2.34										
	E_1 (MV/m)	44.8		10.54	10.89	8.36										
50/50 Irradiated at 120 °C	P_1 (mC/m ²)	87.0	62.5	54.0	47.5	33	-	31.5	-				20			
	P_2 (mC/m ²)	64.4	7.51	3.4	4.90	3.94	-	3.10	-				2.42			
	E_1 (MV/m)	44.8	11.2	5.9	10.45	17.54	-	13.59	-				17.36			
65/35 Irradiated at 25 °C	P_1 (mC/m ²)	105.0						64				65		35		
	P_2 (mC/m ²)	86.38						4.3				5.3		1.98		
	E_1 (MV/m)	55.41						8.1				8.2		5.7		
65/35 Irradiated at 77 °C	P_1 (mC/m ²)	105.0	-	-	-	57.00		50.00		46.5	-	40.00	-			
	P_2 (mC/m ²)	86.38	-	-	-	6.23		4.32		3.38	-	3.41	-			
	E_1 (MV/m)	55.41	-	-	-	13.14		10.17		8.95	-	10.64	-			
65/35 Irradiated at 95 °C	P_1 (mC/m ²)	105.0	-	-	62.00	60.00		53.00								
	P_2 (mC/m ²)	86.38	-	-	4.00	5.56		6.05								
	E_1 (MV/m)	55.41	-	-	7.00	10.78		13.24								
65/35 Irradiated at 120 °C, Ar. Atmosph.	P_1 (mC/m ²)	105.0	-	100.0	66.00	50.00		27.50								
	P_2 (mC/m ²)	86.38	-	58.03	7.77	3.52		3.38								
	E_1 (MV/m)	55.41	-	29.52	11.37	7.77		17.55								

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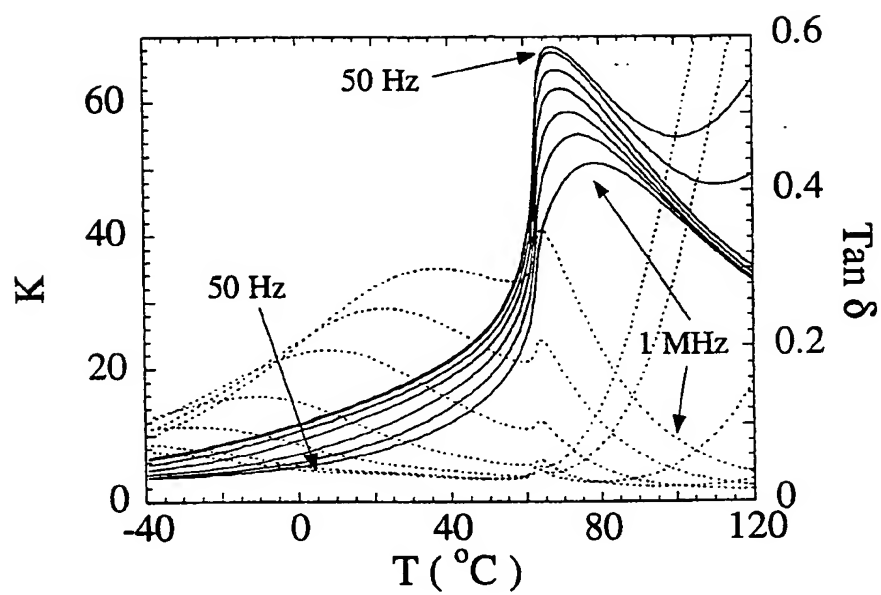


Figure - 8

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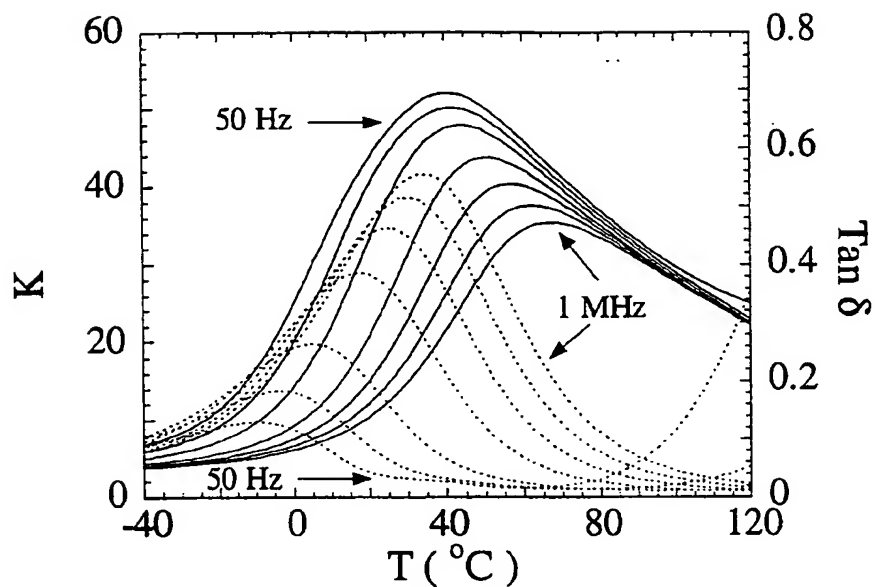


Figure - 9

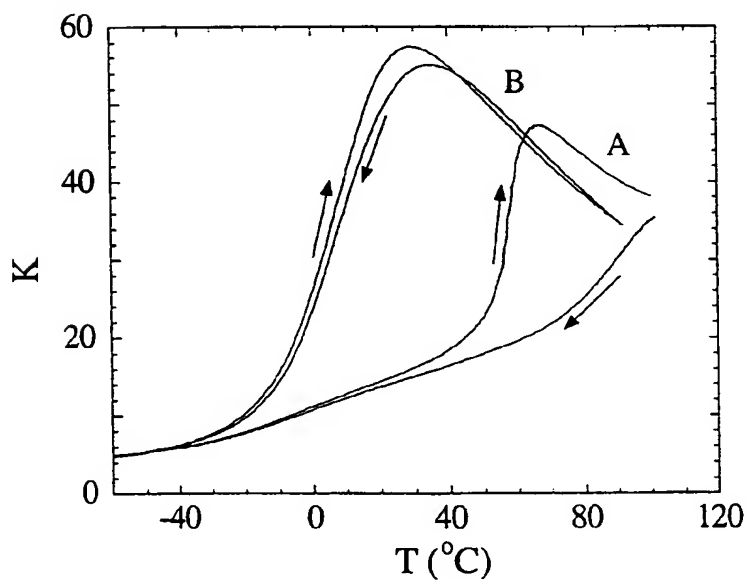


Figure - 10

SUBSTITUTE SHEET (rule 26)

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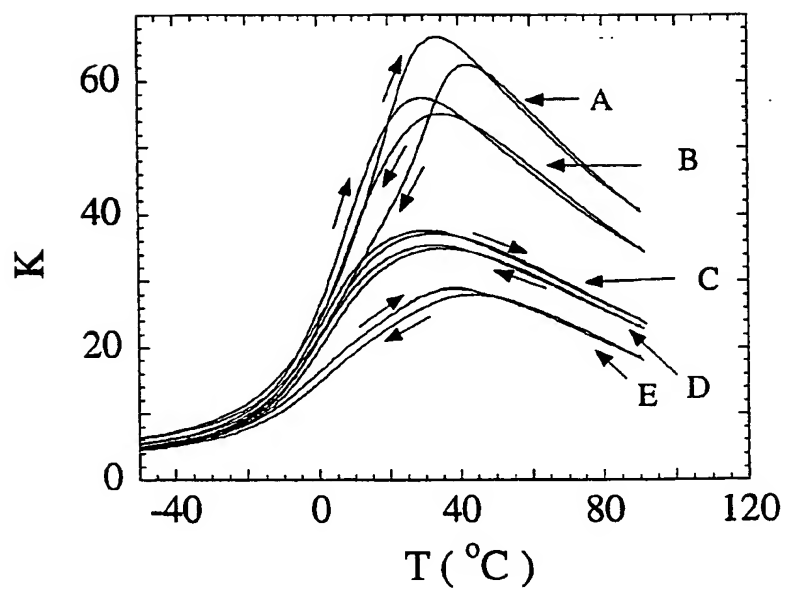


Figure - 11

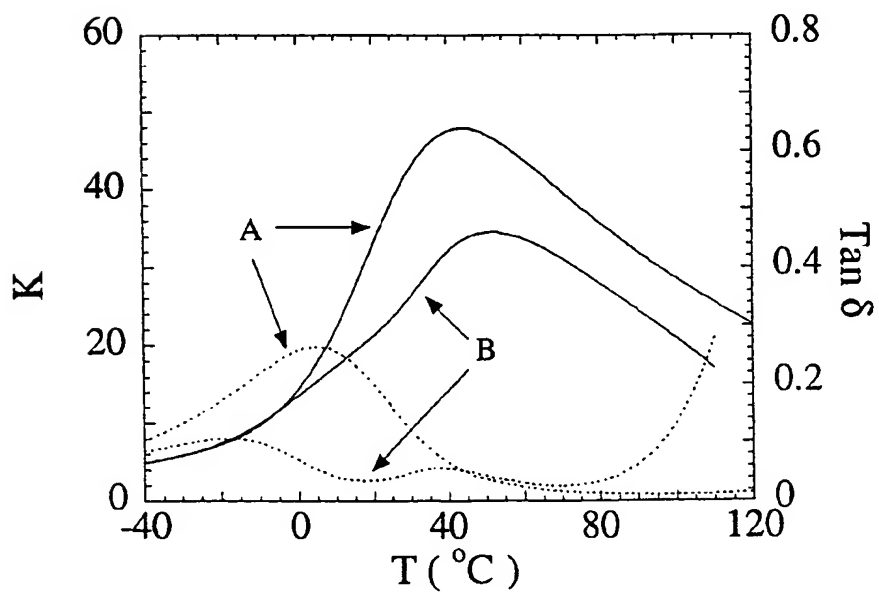


Figure - 12

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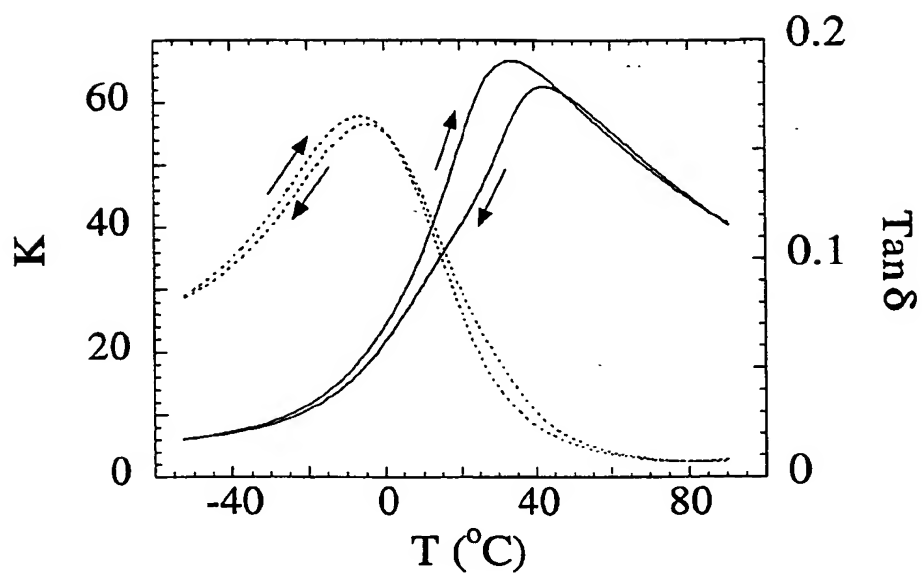


Figure - 13

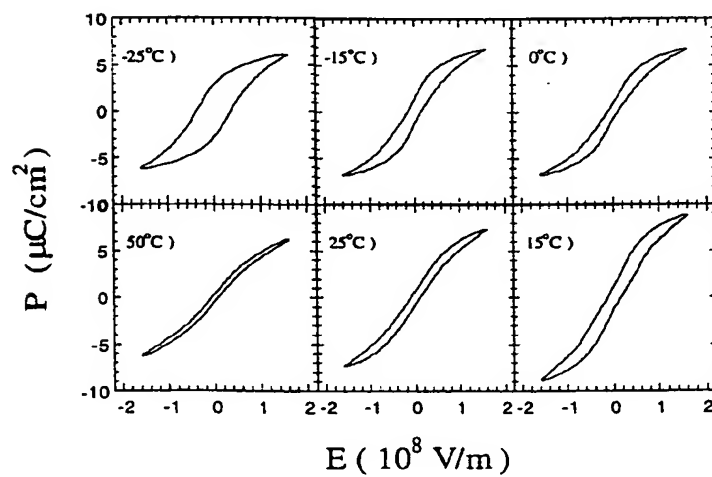


Figure - 14

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Copolymer Film

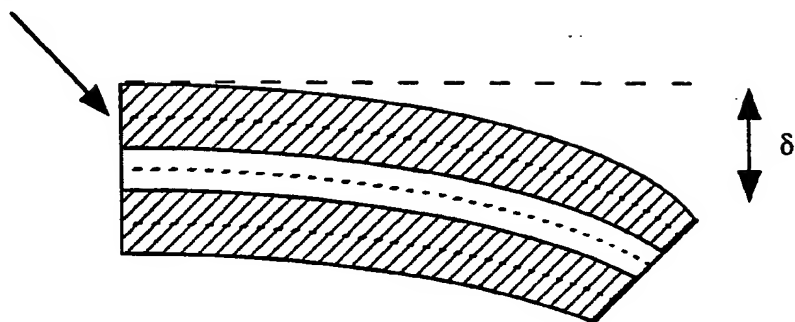


Figure - 15

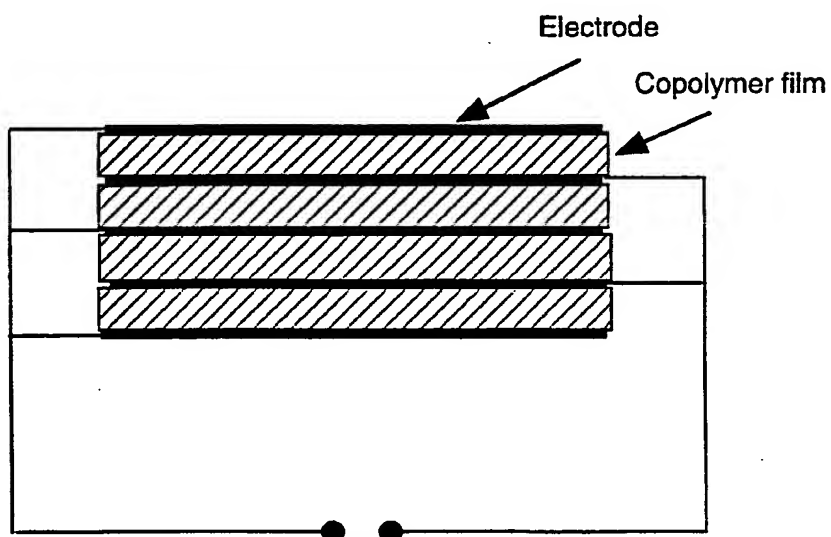


Figure - 16